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ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF METALLURGY --ETC F/6 11/6  
ON THE OXIDATION OF NIOBIUM IN 'PURE' HYDROGEN ATMOSPHERES.(U)  
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B. J. Makenas

ONR Contract USN N00014-75-C-1012  
Technical Report  
October 18, 1977

(See back page  
for 1473)

University of Illinois at Urbana-Champaign  
Department of Metallurgy and Mining Engineering  
Urbana, Illinois 61801

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# On the Oxidation of Niobium in "Pure" Hydrogen Atmospheres

B. J. Makenas

Department of Metallurgy and Mining Engineering

University of Illinois at Urbana-Champaign

Urbana, IL 61801

## INTRODUCTION

In recent years there has been great interest in the behavior of interstitial solutes, particularly hydrogen, in refractory metals. Hydrogen charging procedures often involve the equilibration of specimens with a purified hydrogen atmosphere at pressures determined by the metal-hydrogen equilibrium. Since the refractory metal surface oxides are effective hydrogen permeation barriers, this procedure generally requires equilibration at temperatures greater than 300°C after annealing at about 600°C to dissolve the surface oxide film. Although this procedure has been widely used, the extent of introduction of oxygen impurities has not been established.

Interaction of the refractory metals with  $O_2$  (or  $H_2O$ ) and  $N_2$  has been widely investigated [1,2] over a wide range of temperatures and partial pressures of the reactive gases. In addition to the stable oxides and nitrides a large number of suboxides and subnitrides as well as ordered structures have been reported [3-6]. Suboxides form as precursors to stable oxides either in the early reaction times or at low  $O_2$  (or  $H_2O$ ) partial pressures [7].

In the present study, the formation of these suboxides during low temperature hydrogen annealing will be shown. The suboxide formation will also be shown to result from a hydrogen enhanced oxidation process.

## EXPERIMENTAL PROCEDURE

Transmission Electron Microscopy (TEM) specimens were prepared by electropolishing high purity niobium sheet which had been out-gassed at 2300°C in vacuums of about  $1 \times 10^{-8}$  Pa. After thinning they were equilibrated with atmospheres of  $H_2$ , which had been purified by diffusion through a Pd membrane, in a stainless steel UHV charging system which was initially evacuated to about  $10^{-6}$  Pa. The specimens were examined in a 200 KV JEOL microscope which was equipped with a STEM and both heating and cooling stages. The morphology and structure of the precipitated phases were examined. Attempts to establish the compositions of the precipitates were not successful. The hydrogen concentrations were determined by vacuum extraction methods.

## RESULTS AND DISCUSSION

Anneals at 650°C, the temperature to which specimens are usually heated for hydrogen doping, in vacuums of  $1.3 \times 10^{-6}$  Pa resulted in large numbers of oxides throughout the volume of the specimen. In contrast to this, annealing at 250°C for eighteen hours in a vacuum of  $1.3 \times 10^{-6}$  Pa did not produce any precipitates which were visible in TEM. Similar specimens were then annealed in an atmosphere of 20.8 Pa  $H_2$  for eighteen hours in an attempt to diffuse H through the surface oxide layer. Subsequent analysis showed that  $H/Nb = 0.025$  had been achieved compared to the  $H/Nb = 0.05$  expected from equilibrium with the hydrogen gas. Hydrogen charging can therefore occur by permeation through the surface oxide during long time anneals at low temperatures.



TEM examination of these specimens revealed a high concentration of precipitates in the thinnest part of the foil, within 10  $\mu\text{m}$  of the central perforation as shown in Fig. 1. Each precipitate consisted of alternate domains separated by  $\{110\}_{\text{bcc}}$  boundaries with several boundary orientations often present in a single precipitate. Selected area diffraction patterns, Fig. 2, exhibited a large number of superlattice reflections and could not be indexed with any of the known hydride structures. In situ heating and cooling experiments also showed that these precipitates were not hydrides. Rapid cooling to 77 K did not cause growth of these precipitates although precipitation of  $\beta$  hydride occurred in the thick portion of the foil away from the precipitates. Heating to 250°C in the TEM caused growth of these precipitates similar to that seen by Van Landyt [8] for suboxides. If these had been hydrides, resolution would have occurred [9]. Additional annealing at 400°C at vacuums of  $2.6 \times 10^{-5}$  Pa for 18 hours produced changes in the morphology and structure of the precipitates (Fig. 3).

Apparently an interstitial phase, other than a hydride, forms during annealing of niobium thin foils in a purified hydrogen atmosphere. This phase is most likely a suboxide of niobium. Such suboxides have been seen in the V-O [5], Ta-O [10] and Nb-O [6] systems. They are characterized by diffraction patterns which contain large numbers of superlattice reflections whose spacings are not simple fractions of the normal bcc reciprocal lattice vectors. There is no dislocation structure associated with the suboxides, which usually contain twin boundaries parallel to  $\{110\}$  planes. The twinning results from the multiplicity of the oxide ordering variants (domains)

in which the oxygen sublattice has different orientation relative to the bcc niobium lattice.

Monfort et al [5] have determined the reciprocal lattice for a tetragonal suboxide of niobium ( $\text{Nb}_8\text{O}$  to  $\text{Nb}_{6.5}\text{O}$ ) which they call  $\text{NbO}_x(\text{I})$ . The electron diffraction patterns presented here (Fig. 2) can be satisfactorily interpreted as superpositions of two or more single-domain patterns from this suboxide. Unfortunately, exact oxygen sites for this niobium suboxide structure are not yet available in the literature. Milillo and Potter [11] have recently calculated oxygen positions in tantalum for a very similar, but not identical, suboxide.

It is notable that the formation of the niobium suboxide precipitates occurred only in the presence of purified hydrogen gas. One possible explanation is that the hydrogen aids in the transport of contaminants, principally oxygen, to the niobium sample from the surrounding vacuum system walls. Hickmott [12] has established that, for glass vacuum systems, the presence of hydrogen increases the partial pressure of water vapor. This occurs principally through the formation of atomic hydrogen at hot tungsten ionization gauge filaments and the subsequent reduction, by this hydrogen, of  $\text{SiO}_2$  at the vacuum chamber. It is possible that a similar cycle involving hydrogen reduction of metal oxides at vacuum system walls exists for the stainless steel hydrogen charging system used here. Annealing below  $1600^\circ\text{C}$  in an atmosphere of water vapor is known to irreversibly increase the oxygen concentration of niobium [1] and Monfort et al [6] observed the same suboxide phase identical to that observed in the present work after charging in argon saturated with water vapor at  $305^\circ\text{C}$ .

## CONCLUSION

It has been shown that it is possible to introduce small amounts of hydrogen into thin niobium foils by diffusion of hydrogen through the surface oxide layer at 250°C. However, this method of gaseous charging at elevated temperatures may unavoidably lead to the pickup of oxygen and the formation of suboxide phases in thin foils and at the surface of bulk samples. The presence of hydrogen plays a key role in the transport or dissolution of oxygen.

## ACKNOWLEDGEMENT

The author gratefully acknowledges very helpful discussions with Dr. H. K. Birnbaum and Dr. H. L. Fraser of the University of Illinois. Use of the electron microscopy facility of the Materials Research Laboratory of University of Illinois is also acknowledged. This work was supported by the Office of Naval Research under contract USN N 00014-75-C-1012.

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## REFERENCES

1. E. Fromm: J. Vac. Sci. Technol., 1971, vol. 7, pp. 100-105.
2. E. Fromm and H. Jehn: Vacuum, 1969, vol. 19, pp. 191-197.
3. P. Jung and T. Schober: Scripta Met., 1975, vol. 9, pp. 949-953.
4. D. I. Potter, H. D. Epstein, and B. M. Goldstein: Met. Trans., 1974, vol. 5, pp. 2075-2082.
5. K. Hiraga and M. Hirabayashi: Trans. JIM, 1975, vol. 16, pp. 431-440.
6. Y. Monfort, A. Maisseu, G. Allsis, A. Deschanvres and P. Delavignette: Phys. Stat. Sol., 1973, vol. 15, pp. 129-142.
7. K. A. Jones and R. M. Rose: Acta Met., 1976, vol. 24, pp. 45-51.
8. J. Van Landuyt: Phys. Stat Sol., 1964, vol. 6, pp. 957-973.
9. R. J. Walter and W. T. Chandler: Trans. Met. Soc. AIME, 1965, vol. 233, pp. 762-765.
10. J. Van Landuyt and C. M. Wayman: Acta Met., 1968, vol. 16, pp. 803-813.
11. D. I. Potter: Private Communication, Argonne National Laboratory, Argonne, Illinois.
12. T. W. Hickmott: J. Appl. Phys., 1960, vol. 31, p. 128-136.



## FIGURE CAPTIONS

1. Suboxide precipitates formed in thin foil samples during gaseous hydrogen charging at 20.8 Pa pressure of  $H_2$  and 250°C.
2.  $\{100\}_{bcc}$  selected area diffraction patterns taken from multi-domain suboxide precipitates.
3. Oxide structures which formed during annealing of foils, which previously contained suboxide shown in Fig. 1, for an additional 18 hours at 400°C.

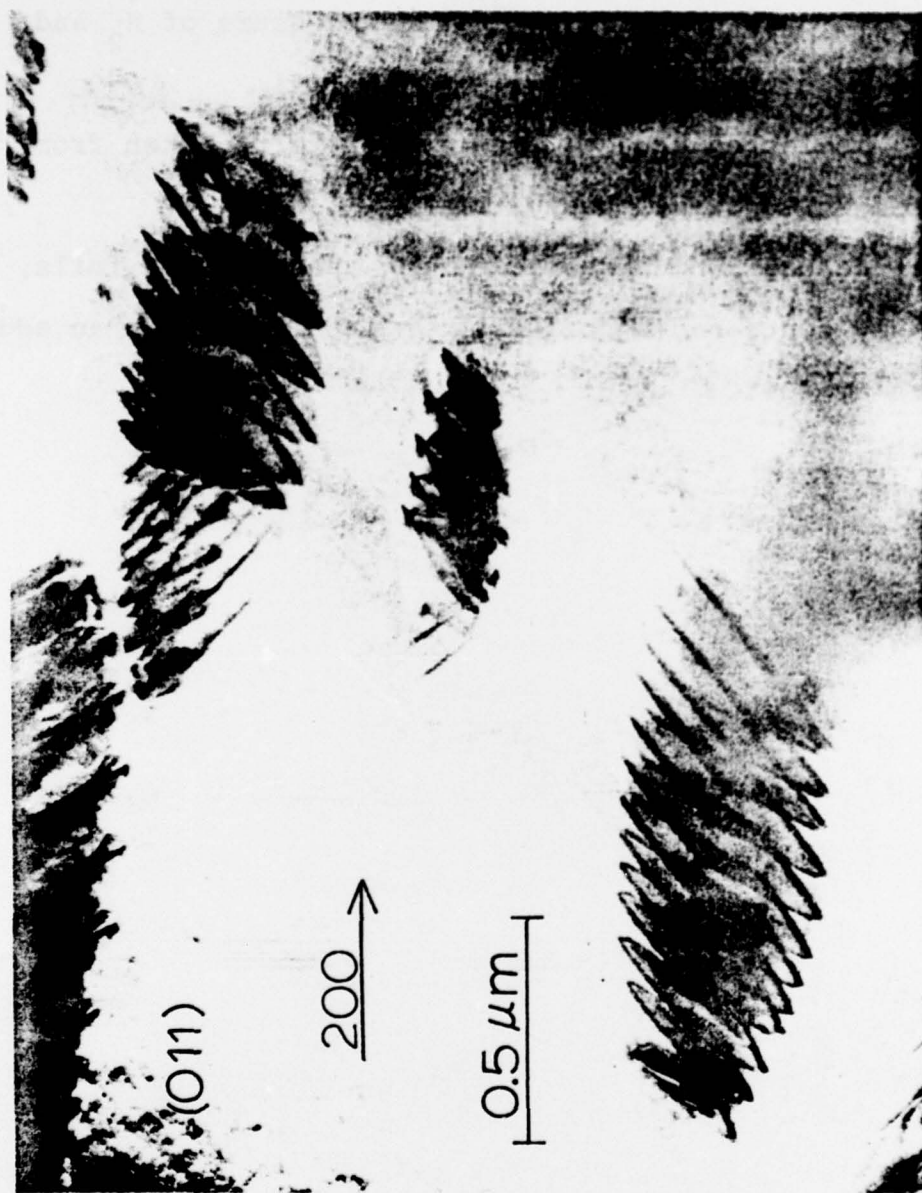


fig.1

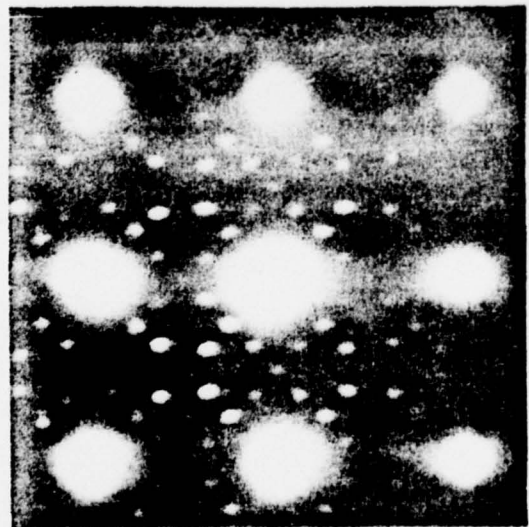
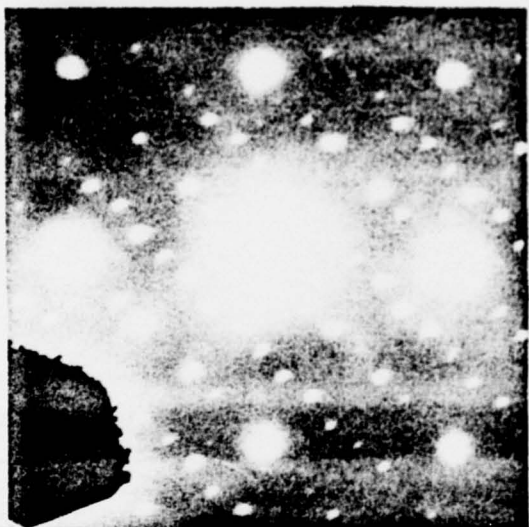
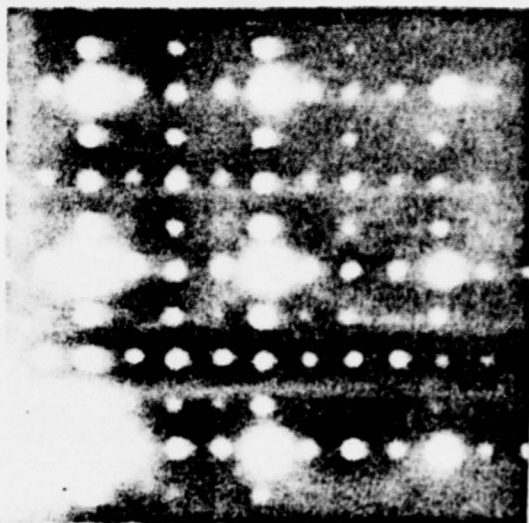


fig. 2

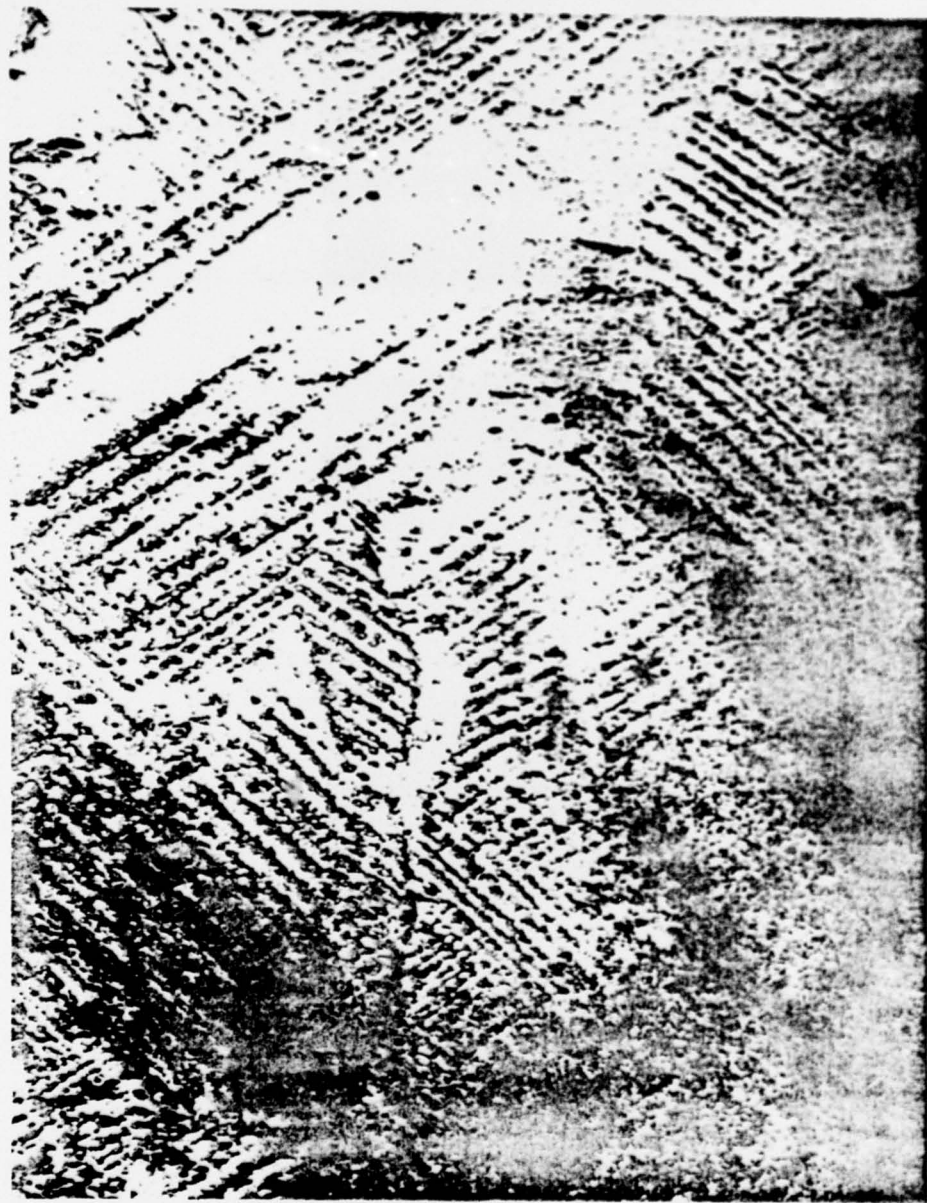


fig. 3



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Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
University of Illinois		UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE			
6 On the Oxidation of Niobium in "Pure" Hydrogen Atmospheres.			
4. DESCRIPTIVE NOTES (Type of report and, inclusive dates)			
9 Technical Report.			
5. AUTHOR(S) (First name, middle initial, last name)			
10 B. J. Makenas			
6. REPORT DATE		7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
October 18, 1977 11 18 Oct 77		11	12
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S)	
15 USN N 00014-75-C-1012			
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
12 16 p.			
10. DISTRIBUTION STATEMENT			
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11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		Office of Naval Research	
13. ABSTRACT			
The oxidation of niobium at very low partial pressures of oxygen was studied using transmission electron microscopy and electron diffraction. The oxidation was carried out in "high purity" hydrogen atmospheres.			
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